ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES IN JAPAN. III. CALCIUM CARBONATE MINERALS DEPOSITED FROM EFFERVESCENT SPRINGS.

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Calcium carbonate when deposited from effervescent springs in Japan, rarely forms a transparent colourless mineral, and in most cases an opaque light-yellow crystalline mass. The latter is frequently contaminated with oxide of iron, sometimes mixed with oxide of manganese, silicic acid, arsenious sulphide etc. Therefore, in almost all cases, the mineral when treated with hydrochloric acid, is reduced to a small insoluble portion, while the larger proportion is dissolved with effervescence.

The mineral presents various forms and appearances, namely, a massive rock, an earthy mass, a small spherical globule, a long fibrous or sometimes white silky crystalline mass, an oolitic group etc. Which of these forms belong to aragonite or calcite, can hardly be distinguished by ordinary optical tests, though the former crystallises in a rhombic system, and the latter in a hexagonal system. At present X-ray analysis is used for the determination of crystalline system, but the apparatus employed being very complex, we often prefer a simpler but pretty accurate method. As is well known, aragonite is greater than calcite in its specific gravity, but it is difficult to estimate its value, for the mineral is of porous structure. Therefore, the author considers that the method discovered by Meigen[1] is most simple and reliable, and he has applied this method to several $CaCO_3$ minerals for the classification of them.

On the author's experiments, calcium carbonate precipitated at a temperature higher than 50°C. forms aragonite, but at a temperature lower than 50°C. it usually forms calcite. Meigen assumes that the necessary cause of the formation of aragonite is decidedly a high temperature, but his assumption is not always correct. If $CaCO_3$ is deposited in an alkaline system, the precipitate becomes aragonite even at a low temperature, while in presence of free carbonic acid or in an acidic system, calcite is always deposited.

(1) W. Meigen, *Centralb. f. Min.*, 1901, 577.

This latter fact was first proposed by Warth,[1] and has been confirmed by the author. For instance, if an insufficient quantity of $CaCl_2$ is added to Na_2CO_3 aq. to precipitate $CaCO_3$ in alkaline system at an ordinary temperature, we obtain aragonitic substance, while on the other hand if a sufficient quantity of $CaCl_2$ is added to $NaHCO_3$ aq. with the constant evolution of CO_2, we obtain calcite, when tested by Meigen's reactions.

Both of these precipitates consist of small crystals with an appearance of rhombohedron, although they are different in Meigen's reactions. One of them which is aragonitic in the reaction, is changed into calcite on the lapse of a few days, or sometimes even a few hours. In this case, Meigen denies the above proposal of Warth, and insists that such a substance with an aragonitic property is not really aragonite, but it is another substance such as *vaterite* for instance.

In fact, this unstable product gives the same reaction as aragonite, but is easily changeable to calcite.

On testing $CaCO_3$ secreted from the several kinds of Mollusca and lime algae by Meigen's method, the author found that most of these products consist of aragonite and ascertained their crystalline structure under microscope. The author has also collected the shells of Mollusca which have been allowed to stand 40 or 50 years, and has proved that they have been preserved as aragonite.

By these facts, it is clear that a high temperature is not necessary to obtain aragonite, in contradiction to Meigen's hypothesis.

The presence of slimy or gelatinous substance in the shells of Mollusca is also a noticeable fact, and the author comes to consider that this cementing substance is highly related to the formation of aragonite.

On the author's experiments, 1%–2% solution of gelatin is mixed with unstable aragonitic precipitate freshly prepared in a cold alkaline system, and is allowed to stand for a few months, in order to examine wheather the transformation of the above named precipitate into calcite is usual or not. After one, two or more months, the precipitate reacts aragonitic, i. e. its reaction is constant. The material treated as above is almost the same in appearance as the substance first taken, but is different in its stability, because the substance is no more unstable but exactly the same as ordinary aragonite.

Thus it is possible to obtain ordinary aragonite by precipitation at a low temperature in presence of gelatin. Generally, a gelatin solution is known as a protective colloid, and it seems to favour the formation of real aragonite.

(1) H. Warth, *Centralb. f. Min.*, 1902, 492.

Calcite is more stable than aragonite; therefore, the former is never changed into aragonite in the solution of gelatine. The author determined the value of P_H of both the solutions which had been prepared by boiling native aragonite and native calcite with distilled water. The result is as follows:—

Mineral.	P_H by electric method.	P_H by indicator method
Aragonite	8.2	8.4
Calcite	7.6	8.0

This shows also that there predominates the unstability or solubility of aragonite, because its hydrolysis depends upon the greater solubility.

Further the reactions of Meigen exactly coincide to the above results, i. e. on boiling the powder of aragonite with a dilute solution of $Co(NO_3)_2$, the powder is coloured violet, a basic cobalt carbonate being formed, while calcite is coloured sky-blue on long boiling with the same reagent, probably anhydrous cobalt carbonate being formed.

Furthermore, the aragonite powder suspended in water is coloured green by the addition of green vitriol, a basic ferrous sulphate being formed, while calcite on the same treatment is coloured yellow, at first probably the acidic solution of $FeSO_4$ being neutralized, and then ferric oxy-sulphate being formed by the oxydizing action of atmospheric oxygen.

It is probable that when carbonates are mixed with the solution of magnesium salts, magnesium carbonate is more or less produced, and the latter, which hydrolyses on dissolving in water, presents a noticeable alkaline reaction in the solution.

For the above reason, an effervescent spring and also sea water containing some magnesium salts have slight alkaline reactions, and have naturally a tendency of forming aragonite when $CaCO_3$ is precipitated in them.

Lastly, aragonite produced in hot springs frequently has a granular or oolitic form. Probably this is caused by the following functions:—

(1) The nucleus of the granule is deposited first with the evolution of CO_2 gas.

(2) Edges or tops of crystals are mostly dissolved by carbonic acid or are ground by mechanical revolution in water current.

Thus the precipitate becomes spherical and grows gradually through the decomposition of $Ca(HCO_3)_2$ as shown by the following equation:—

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

This conclusion is reached by the zonal structure of spherical grobules as well as by the etch figures on their surfaces with the consideration that they are formed by a dissolving action of carbonic acid.

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ON ENANTIOTROPY AND MONOTROPY. I.

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It can be considered that any polymorphism, including the cases where the number of modifications exceeds two, is composed of pairs of dimorphisms. The behaviours of dimorphism, therefore, play the fundamental rôle in the study of polymorphism. O. Lehmann[1] was the first in classifying dimorphism into two distinct categories, enantiotropy and monotropy. He stated: "Die charakteristische Eigentümlichkeit enantiotroper Modifikationen besteht in der Umkehrbarkeit des Umwandlungsvorganges bei der *normalen* Umwandlungstemperatur. . . . . Ganz wesentlich verschieden hiervon verhalten sich die monotropen Modifikationen. . . . . , denn die Umwandlung ist nicht umkehrbar, irreversibel. Bei dieser Klasse von Körpern existiert also eine im festen Zustande stets stabile und eine stets labile Modifikation, von welchen sich unter allen Umständen nur die letztere in die erstere umwandelt und zwar unter Freiwerden von Wärme." Later some interpretations on this subject were made by Ostwald, Schaum, Roozeboom, Tammann and others, on the basis of the phase theory.[2] The definitions of the terms, enantiotropy and monotropy, however, have not been made which are consistent with the experimental cases. On this point, much ambiguities and incompleteness were found by the author. One of the chief objects of this paper is to make clear the definitions for them as well as the thermodynamic relations connected to them.

Definitions of Enantiotropy and Monotropy. The fundamental idea of O.Lehmann is to classify the behaviours of dimorphism, "under the atmospheric pressure" or "at the *normal* pressure", into two categories, enantiotropy and monotropy. We may, however, extend it more generally for the cases "at constant pressure." Some dimorphism which is enantiotropic or monotropic at one atmospheric pressure may change into the other by the effect of pressure.[3] It is, therefore, necessary to add the condition of pressure or the range of pressure when we express in such cases, the relations of stability in terms of enantiotropy and monotropy.

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(1) O. Lehmann, "Molekularphysik" (1888), I, p. 193.

(2) Wilh. Ostwald, *Z. physik. Chem.*, **22** (1897), 313; Schaum, *Lieb. Ann.* **300** (1897), 215; H.W.B. Roozeboom, "Die heterogenen Gleichgewichte" (1901), I, pp. 109, 159; G. Tammann, "Kristallisieren und Schmelzen" (1903), p. 101.

(3) O. Lehmann gave no remarks on the effects of pressure on the stability of dimorphism as is clear in the quotation given above.

Let us now interpret more closely the term, "transition." Two types of transition are probable. One is the case in which it occurs from the metastable to the stable[1] modification, the other is the case in which it occurs from the metastable to the metastable modification. In general, the first case occurs in nature. And as the experimental fact, fairly smooth phase changes occur from the solid to the liquid or the gaseous phase. Hence, in the use of the terms enantiotropy and monotropy, it will be convenient to confine it only in such cases, in which the transition occurs from the metastable to the stable modification and the phase changes from the two modifications to any other phases are free from the effects of pseudequilibrium.

We may now define enantiotropy by the following two conditions at constant pressure:

(1) There should be (neutral) equilibrium temperature between the two modifications A and B in one component.[2]

(2) In the neighbourhood thereof, A should be stable above it, B being stable below it, or vice versa.

The dimorphism which does not satisfy the above conditions at constant pressure is defined to be monotropy, if only one of the two modifications is stable. With the above conditions in mind, we are able to consider that monotropy is included in the following cases:

(i) The dimorphism without any equilibrium temperature.[3]

(ii) The dimorphism with equilibrium temperature only in the unstable domain of A and B.

(iii) The dimorphism with equilibrium temperature, however, only A (or B) is stable except there.

By means of a few examples these definitions will be more clear. The schematically drawn pT-diagrams[4] of sulphur, methylene iodide and phenol are shown in Fig. 1, Fig. 2 and Fig. 3 respectively. Fig. 1 is the case in which the enantiotropic dimorphism at one atmospheric pressure changes into the monotropic at high pressure. Fig. 2 is the case in which the monotropic dimorphism at low pressure changes into the enantiotropic at high pressure. In Fig. 3 we found one of the examples with two transition points at constant pressure.

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(1) The term "stable" will be used in the sense of "more stable than any other phases."

(2) When clear, the condition of "one component" will be omitted. And the two modifications will be considered to satisfiy the condition of "pure homogeneous phase".

(3) After the general customs of the study in this field, equilibrium temperature is considered even in the unstable domain. Monotropy (i) is the case in which such temperature cannot be considered both in the stable and unstable domains of the two modifications.

(4) G. Tammann, loc. cit. p. 270 (sulphur); p. 280 (methylene iodide): p. 310 (phenol). As for methylene iodide, cf., A.H.R. Müller, *Z. physik. Chem.*, **86** (1913), 237.

In our definitions, it is enantiotropic at P_2 in Fig. 1 and at P_3 in Fig. 2. At P_1 and P_2 in Fig. 3 we have the enantiotropy with two transition points. At P_1 one of the transition points lies in the unstable domain, the rest being in the stable domain. It may be mentioned here that it cannot always be monotropic even if one of the transition points lies in the unstable domain. At P_4 in Fig. 3 we have one of the examples for monotropy (i), and at P_3 in Fig. 1 and at P_2 in Fig. 2, monotropy (ii), and also at P_3 in Fig. 3, monotropy (iii). It is evident that we have always monotropy (iii) and (ii), at and below the pressure of the triple point among two solids and gas, as at P_1 in Fig. 1 and Fig. 2. And also we have monotropy (iii) at the pressure of the triple point among two solids and liquid in Fig. 1 and Fig. 2.

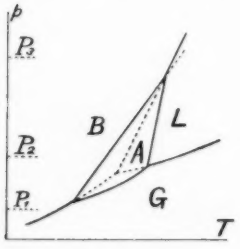

Fig. 1.

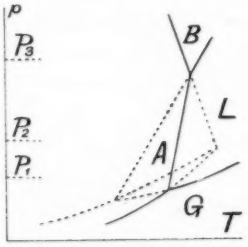

Fig. 2.

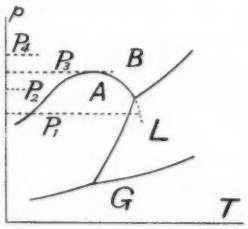

Fig. 3.

Criteria of Mutual Stability and Equilibrium. In the pT-diagram, the most convenient criteria for equilibrium and stability is the Gibbs' ζ-function. In order to know the mutual stability of the two modifications A and B at the point (pT), we have to consider the difference Z of the specific values of ζ-fuction for A and B.

$$Z = \zeta_B - \zeta_A, \quad \text{or} \quad Z = X - Q,$$

where X is the heat absorbed when the transition occurs naturally from A to B at constant temperature and pressure, or the calorimetric heat of transition; and Q is the heat absorbed when it is made in the reversible way at constant temperature.

A and B are in equilibrium when $Z=0$, or $X=Q$. It is clear that A is more stable than B when $Z>0$, or $X>Q$, for such a change cannot occur in nature in which the calorimetric heat is greater than that of the reversible change as before. And also B is more stable than A when $Z<0$, or $X<Q$.

At constant pressure, we have $Z=f(T)$, or Z varies only with the variation of temperature along the curve $f(T)$. If we let the equilibrium temperatures be T_0 T_0' , ... etc., we have these as the roots of the equation $f(T)=0$, or $Z=0$. It is, therefore, necessary to investigate the nature of the equation $f(T)=0$, or the nature of the Z-curve, in order to find the equilibrium

point as well as to know the relation of mutual stability in the given dimorphism at constant pressure.

We have monotropy (i) if there is no real root in the equation $Z=0$, and only one modification is stable. If there is one real and positive root T_0 in the equation $Z=0$, the behaviour of the Z-curve will be as in Fig. 4.

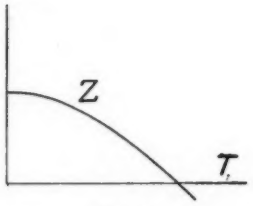

Fig. 4.

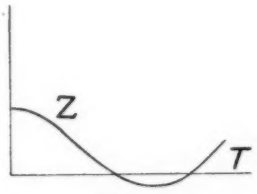

Fig. 5.

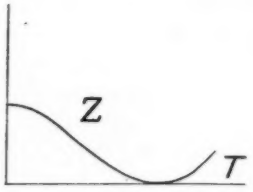

Fig. 6.

If there is only one melting point for each modification at constant pressure, we shall have monotropy (ii) when T_0 lies above the melting point; and also enantiotropy, when below. We shall next consider the cases with two real and positive roots in the equation $Z=0$, each modification having only one melting point. In these cases, we shall have in general enantiotropy or monotropy (ii) as before. The behaviour of the Z-curve is as in Fig. 5. However, if the two roots are equal, the Z-curve will be brought in contact with the T-axis as in Fig. 6, which is the case at P_3 in Fig. 3. In this case, the two modifications have an equilibrium point. However, if the transition is made to occur directly[1] at the pressure under considerations, it shall be limited in one direction as in monotropy (i) and (ii). It is not enantiotropic and may be ascribed to monotropy (iii).[2]

We may therefore consider enantiotropy,[2] on the basis of thermodynamics, as follows; It shall be enantiotropic when Z-curve cuts T-axis between the stable domain of the two modifications. In which case, the direct transition shall occur in two opposite directions above and below the transition point.

Besides above cases, we may be able to consider lots of special cases and the cases in which two melting points exist for each modification at constant pressure. However, these cases are omitted here, for the sake of brevity and owing to the lack of the experimental examples.

Some Theories hitherto Proposed on Enantiotropy and Monotropy and the Cases of Pseudequilibriums. It was first proposed by Ostwald[3] that

(1) We have to add the condition, "directly", or "without any intermediate states including ion." For instance, the red phosphorus changes into the white when heated and distilled. Whereas these modifications stand in the relation of monotropy under the atmospheric pressure.

(2) Monotropy (Gr. *monos*—single; *tropos, trepein*—to change) and enantiotropy (Gr. *enantios*—opposite; *tropos, trepein*—to change).

(3) Wilh. Ostwald, loc. cit.

it is enantiotropic or monotropic according as the transtion point lies below or above the melting point. It is implied in this statement that, under the atmospheric pressure, there is only one melting point for each modification, and one transition point between the two modifications, which is an experimental rule adopted by many authors. Our monotropy (i) and (iii) were not included here. The category of pseudomonotropy was proposed by Roozeboom,[1] in order to make more complete the Ostwald's theory on monotropy, in which following cases were included:

(a) The dimorphism with its transition point in the low temperature where the transition is retarded. In which cases, it may manifest itself like monotropic.

(b) The dimorphism with the equilibrium point at absolute zero.

In the foregoing paragraphs, such cases have been excluded in which the phase changes from the two modifications to any other phases are disturbed by the effects of pseudequilibrium. It is, however, probable that there are the cases in which the dimorphism appears like enantiotropic by such effects which may be called pseudenantiotropy. It is also probable that there are the cases which appear like monotropic and yet can not be classified in our monotropy. It may be called pseudomonotropy. In which the case of (a) in the pseudomonotropy of Roozeboom may be included although it is not necessary to distinguish it from enantiotropy from the thermodynamic standpoint. The case of (b) is nothing but the special case of our monotropy (iii). It may be added here that in the cases of pseudenantiotropy and pseudomonotropy the effects of pseudequilibrium or retardation are necessary.

In a later paper, it will be discussed how our Z-function varies with the temperature and pressure in conjunction with the measurable quantities, and some ambiguous or abstruse cases will be treated.

In conclusion, I would express my hearty thanks to Prof. J. Sameshima whose counsels have been constantly at my disposal.

Summary.

It is a well known fact that there are two distinct behaviours of dimorphism in which transitions are of reversible and irreversible natures. O. Lehmann was the first in classifying it by the two categories, enantiotropy and monotropy. Later it was interpreted by Ostwald and others on the basis of the phase theory. However, clear definitions have not been made so far, which are consistent with all the experimental cases in the wide range of pT-diagram. To make it more complete and concrete, some definitions are

(1) H.W.B. Roozeboom, loc. cit., p. 177.

given for the terms enantiotropy and monotropy. These terms not only serve to express the absolute stability but also to express the mutual stability of the two modifications in one component. The thermodynamic relations connected to them are also described. The cases of pseudequilibrium are also spoken of. As the result of these considerations, various theories on enantiotropy and monotropy are brought into one conformity.

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ON THE OXIDATION OF THE MIXTURE OF STANNOUS HYDROXIDE AND SODIUM SULPHITE IN SODIUM CARBONATE SOLUTION WITH AIR.

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Introduction. It was observed that the mixture of sodium sulphite and stannous hydroxide in sodium hydroxide solution oxidizes very slowly first with air, when the initial concentration of stannous hydroxide is small.[1] The author has an opinion to explain the fact by the transference of active states.[2] If we accept the idea that the active states of the molecules of sodium sulphite transfers to the molecules of stannous hydroxide, it is easy to explain the experimental results as follows.

When the concentration of stannous hydroxide is very small, the oxidation velocity of the mixture with air should be very small first, for stannous hydroxide oxidizes alone, if the active states of the molecules of sodium sulphite transfer to the molecules of stannous hydroxide. After the disappearance of the molecules of stannous hydroxide by the oxidation, sodium sulphite begins to oxidize and the oxidation velocity of the mixture increases. Thus the oxidation of the mixture in sodium hydroxide solution, which will be regarded as a kind of negative induced reaction, can be explained by the transference of active states.

According to this idea, the mixture of sodium sulphite and stannous hydroxide in sodium carbonate solution, should oxidize very slowly, for the oxidation velocity of stannous hydroxide in sodium carbonate solution[3] is very small, though sodium sulphite oxidizes quickly, if it be alone.[4] The present reseach was carred out to ascertain this idea.

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(1) S. Miyamoto, this journal, **2** (1927), 196.
(2) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, **4** (1926), 259
(3) S. Miyamoto, this journal, **3** (1928), 43.
(4) S. Miyamoto, ibid., **3** (1928), 76.

Experimental: The experimental procedure was quite the same as that employed in the previous study on the oxidation of the mixture in sodium hydroxide solution.[1] In the following Tables, v is the volume of sodium thiosulphate solution of 0.0996 normal which is equivalent to the total amount of sodium sulphite and stannous chloride, $v_{0(SnCl_2)}$ and $v_{0(Na_2SO_3)}$ being the initial amounts of stannous chloride and sodium sulphite respectively.

If the oxidation of stannous hydroxide take place alone, v should have the value v' given in the following tables, which was calculated by $v' = v_0 - k't$, k' being the velocity constant of the oxidation of stannous hydroxide in sodium carbonate solution given in the previous paper.

If sodium sulphite oxidize alone, v should have the value v'' given in the following tables, which was calculated by $v'' = v_0 - k''t$, k'' being the velocity constant of the oxidation of sodium sulphite and calculated by $k = 0.258 - 0.114\ C_{Na_2CO_3}$, given in the previous paper.

TABLE 1.

Temp.=20°C. $C_{Na_2CO_3}$=0.2780 normal.
Velocity of air=7.78 litres per hour.

$v_{0(SnCl_2)}$ c.c.	$v_{0(Na_2SO_3)}$ c.c.	t min.	v c.c.	v' c.c.	v'' c.c.
12.98	2.89	0	15.87	—	—
		15	15.73	15.77	—
		30	15.70	15.66	—
		60	15.62	15.46	—
8.14	11.32	0	19.46	—	—
		10	19.30	19.39	17.20
		30	19.19	19.25	12.68
		60	19.05	19.05	5.90
1.69	19.82	0	21.51	—	—
		10	21.39	21.44	19.25
		40	21.09	21.23	12.47
		60	21.03	21.10	7.95
0.42	13.72	0	14.14	—	—
		10	13.95	—	11.88
		30	13.75	—	7.36
		60	13.47	—	0.58
0.13	20.48	0	20.61	—	—
		10	20.06	—	18.35
		50	20.03	—	9.31
0.031	15.33	0	15.36	—	—
		10	15.20	—	13.10
		30	10.95	—	8.57
		60	5.46	—	1.80

(1) Loc. cit.

TABLE 2.

Temp.=20°C. $C_{Na_2CO_3}$=0.4655 normal.
Velocity of air=7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	v' c.c.	v'' c.c.
16.74	1.21	0	17.95	—	—
		10	17.90	17.88	—
		30	17.80	17.74	—
		60	17.68	17.54	—
7.93	10.71	0	18.64	—	—
		10	18.56	18.57	16.59
		30	18.40	18.43	12.49
		60	18.29	18.23	6.34
1.66	13.71	0	15.37	—	—
		15	15.19	15.27	12.29
		35	14.99	15.13	8.19
		60	14.85	14.96	3.07
0.44	18.25	0	18.69	—	—
		10	18.48	—	16.64
		60	18.20	—	6.39
0.12	16.37	0	16.49	—	—
		10	16.17	—	14.44
		30	15.85	—	10.34
		60	15.78	—	4.19
0.024	16.22	0	16.24	—	—
		8	16.15	—	14.60
		25	12.75	—	11.11
		50	8.29	—	5.99

It seems from Table 1 and 2, that stannous hydroxide alone is oxidized, when air is passed into the mixture in sodium carbonate solution, as is expected. When the initial concentration of stannous hydroxide is very small, the mixture is oxidized very slowly first and increases afterwards, as is shown in the Tables. The result is easily explained quite the same way as in the case of the oxidation of the mixture in sodium hydroxide solution, by accepting the idea above described.

Thus the oxidation of the mixture of stannous hydroxide and sodium sulphite is an example of negative induced reaction; the oxidation of the first substance has an inhibiting action on the oxidation of the second one. The mechanism of the reaction can be explained by the transference of active states.[1]

Summary.

1. The oxidation of the mixture of sodium sulphite and stannous hydroxide in sodium carbonate solution was studied.

(1) Loc. cit.

2. It was observed that the reaction is an example of negative induced reaction; the oxidation of stannous hydroxide has an inhibiting action on the oxidation of sodium sulphite.

3. The mechanism of the reaction was discussed.

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO SODIUM HYDROXIDE, SODIUM CARBONATE AND HYDROCHLORIC ACID SOLUTION.

By **Susumu MIYAMOTO.**

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Studies on the oxidation velocities by means of air of several substances, such as ferrous hydroxide,[1] sodium sulphite,[2] stannous hydroxide,[3] and the mixture of sodium sulphite and stannous hydroxide[4] in sodium hydroxide solution, stannous chloride in hydrochloric acid solution,[5] stannous hydroxide,[6] sodium sulphite,[7] and the mixture of sodium sulphite and stannous hydroxide[8] in sodium carbonate solution, were carried out.

This kind of heterogeneous reactions can be considered to take place in three stages, firstly, a part of the molecules of oxygen, which strike the surface of air bubbles, enters into the liquid surface film, secondly, the oxidation occurs in the liquid phase (principally in the surface film), thirdly, the reacting substances in the inner liquid phase diffuse to the surface of the bubbles, and the oxygen dissolved in the surface film diffuses into the inner liquid phase. The slowest process will determine the velocities of these heterogeneous reactions. If the second or the third process be the slowest, the oxidation velocity should depend on the concentrations of the reacting substances. If sufficient reacting substances be always present to react with oxygen as soon as it enters in the surface film, that is, if the concentration of oxygen in the surface film be always kept zero, the apparent oxidation

(1) This journal, **2** (1927), 40.
(2) Ibid., **2** (1927), 74.
(3) Ibid., **2** (1927), 155.
(4) Ibid., **2** (1927), 191.
(5) Ibid., **2** (1927), 259.
(6) Ibid., **3** (1928), 43.
(7) Ibid., **3** (1928), 76.
(8) Ibid., **3** (1928), 95.

velocity is no other than the rate of the first process, the dissolution of oxygen, and will be independent of the concentration of the reacting substances, if the partial pressure of oxygen be kept constant.

Under these conditions, the meaning of the dissolution velocity of oxygen is quite different from that of the dissolution velocity of solid substances in the liquid phase, in which case the process of diffusion governs the velocity. The oxidation velocities of the substances above described with air were almost in every case independent of the concentrations of the reacting substances under the conditions of the author's measurements, if the initial concentrations of the reacting substances be not very small. In these cases, the observed apparent oxidation velocities do not mean the true oxidation velocities of the substances, but the dissolution velocity of oxygen, the meaning of which being above described, into the liquid phase. It is then possible to calculate the approximate values of the dissolution velocity of oxygen into sodium hydroxide, sodium carbonate and hydrochloric acid solution, when air was passed into 40 c.c. of the solution in a test tube (diameter $\fallingdotseq$ 3 cm.) through a glass tube (inside diameter $\fallingdotseq$ 4 mm., outside diameter $\fallingdotseq$ 6 mm.) at the rate of 7.78 litres per hour, from the results of the author's studies. The calculated values are given in Table 1. The concentrations are given in the first column and the dissolution velocities in the second, the third, and the fourth column, some of them being already given in the previous papers.

The results are also shown graphically in Fig. 1.

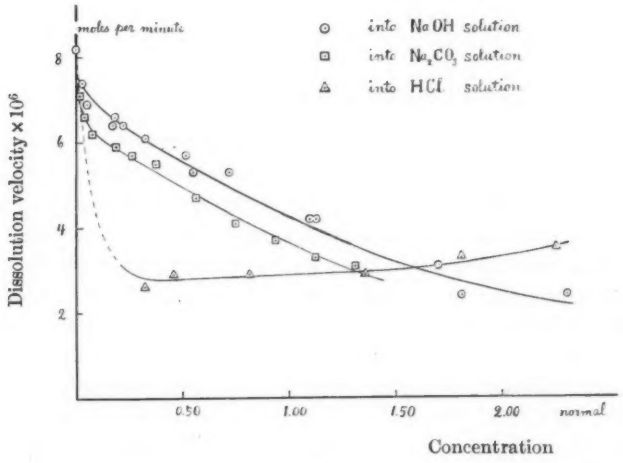

Fig. 1.

TABLE 1.

Temp. = 20°C.

Concentrations normal	Dissolution Velocity of Oxygen × 10^6 moles per min.		
	in NaOH	in Na_2CO_3	in HCl
0	8.2(1)	8.2(1)	8.2(1)
0.01875	—	7.1(1)	—
0.02888	7.4(1)	—	—
0.03750	—	6.6(1)	—
0.05173	6.9(1)	—	—
0.0750	—	6.2(1)	—
0.1706	6.4(2)	—	—
0.1810	6.6(1)	—	—
0.1875	—	5.9(1)	—
0.2204	6.4(2)	—	—
0.2625	—	5.7(1)	—
0.3235	—	—	2.6(3)
0.3252	6.1(2)	—	—
0.3750	—	5.5(1)	—
0.4587	—	—	2.9(3)
0.5173	5.7(1)	—	—
0.5500	5.3(2)	—	—
0.5630	—	4.7(1)	—
0.7219	5.3(1)	—	—
0.750	—	4.1(1)	—
0.8151	—	—	2.9(3)
0.938	—	3.7(1)	—
1.1011	4.2(1)	—	—
1.125	—	3.3(1)	—
1.130	4.2(2)	—	—
1.313	—	3.1(1)	—
1.360	—	—	2.9(3)
1.704	3.1(2)	—	—
1.810	2.4(1)	—	—
1.811	—	—	3.3(3)
2.262	—	—	3.5(3)
2.312	2.4(2)	—	—

(1) The values calculated from the oxidation velocity of sodium sulphite.
(2) " " " " " stannous hydroxide.
(3) " " " " " stannous chloride.

Ferrous hydroxide in sodium hydroxide solution and stannous hydroxide in sodium carbonate solution exist as solid phase in the system and the mechanism of the oxidation of them will be more complex, and the experimental results are not sufficient to discuss it precisely, but from the experimental results, the apparent oxidation velocity of the former seems to be the dissolution velocity of oxygen and that of the latter the reacting velocity.

The author has an opinion to explain some catalysis and induced reaction by the transference of active states.(1) It was ascertained that the increase of the velocity of the induced oxidation of some carbohydrates in the presence of ferrous hydroxide or sodium sulphite with the increase of

(1) *Scientific Papers of the Institute of Physical and Chemical Research*, 4 (1926), 257.

the concentration of sodium hydroxide, studied by C.C. Palit and N. R. Dhar,[1] is not due to the increase of the velocity of the primary reaction; the oxidation velocity of ferrous hydroxide[2] or sodium sulphite[3] decreases with the increase of the concentration of sodium hydroxide. The phenomenon can easily be explained by the transference of the active states of the molecules of the products or the reacting substances of the primary reaction to the molecules of the reacting substances of the secondary reaction.

As was discussed already in the previous papers, the oxidation of the mixture of stannous hydroxide and sodium sulphite can be regarded as a kind of negative induced reactions; the oxidation velocity of sodium sulphite is extremely small in the presence of stannous hydroxide.

According to the author's opinion, some negative induced reactions are explained by the transference of the active states of the molecules of the reacting substances of the secondary reaction to the molecules of some reacting substances or reaction products of the primary reaction, and the oxidation velocity of the mixture studied can be explained by the transference of the active states of the molecules of sodium sulphite to the molecules of stannous hydroxide. The transference of the active states of the molecules of sodium sulphite to the molecules of other substances seems to occur easily, which will be the cause of the existence of many negative catalysers[4] on the oxidation of sodium sulphite.

The catalytic effect of inert gases on some reactions under the influence of alpha-particles, studied by S. C. Lind and D. C. Bardwell,[5] is an experimental result favourable to the author's theory. The phenomenon can be explained as the result of the transference of active states of the molecules of inert gases, excited by alpha-particles, to the molecules of the reacting substances.

Summary.

1. The dissolution velocity of oxygen when air was passed into sodium hydroxide, sodium carbonate and hydrochloric acid solution under some conditions was calculated from the oxidation velocities of sodium sulphite, stannous hydroxide and stannous chloride.

2. The mechanism of some negative induced reactions was discussed.

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(1) *J. Phys. Chem.*, **29** (1925), 799; **30** (1926), 939
(2) Loc. cit.
(3) Loc. cit.
(4) S. L. Bigelow, *Z. physik. Chem.*, **26** (1898), 493; A. Titoff, *Z. physik. Chem.*, **45** (1903), 641; S.W. Young, *J. Am. Chem. Soc.*, **24** (1902), 297.
(5) *J. Am. Chem. Soc.*, **48** (1926), 1575.

SYNTHESIS OF DIETHYL β-METHYL-α, γ-DICYANOGLUTACONATE.

By Yoshiyuki URUSHIBARA.

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Diethyl β-methyl-α, γ-dicyanoglutaconate could not be obtained by the reaction of ethyl sodio-cyanoacetate and ethyl α-cyanoacetoacetate.[1] The formation of the same substance can not be expected in the reaction of methylchloroform with ethyl cyanoacetate in the presence of sodium ethylate, for it is known that methylchloroform does not react with diethyl malonate in the presence of sodium ethylate.

The condensation of ethyl ethoxy-ethylidene-cyanoacetate (ethyl β-ethoxy-α-cyanocrotonate) $CH_3{\cdot}C(OC_2H_5)=C(CN)COOC_2H_5$ with ethyl sodio-cyanoacetate has been tried with success. In this reaction diethyl α-sodio-β-methyl-α, γ-dicyanoglutaconate is produced according to the following equation :

$$C_2H_5OCO(CN)CHNa + C_2H_5OC(CH_3)=C(CN)COOC_2H_5$$
$$= C_2H_5OCO(CN)CNa{-}C(CH_3)=C(CN)COOC_2H_5 + C_2H_5OH,$$

and from it diethyl β-methyl-α, γ-dicyanoglutaconate $C_2H_5OCO(CN)CH{-}C(CH_3)=C(CN)COOC_2H_5$ is obtained by the action of dilute hydrochloric acid.

In a previous paper[2] the author described the synthesis of the nitrile-esters of dicarboxyglutaconic acid by similar condensations, in which ethoxy-methylene compounds were used instead of the ethoxy-ethylidene compound. Thus it has been ascertained that the reaction represented by the following general equation can take place :

$$XYCHNa + ROCR'=CX'Y' = XYCNa{-}CR'=CX'Y' + ROH,$$

where R represents any alkyl group, R′ hydrogen or any alkyl group, and X,X′,Y,Y′ negative groups such as CN or $COOC_2H_5$. It seems possible that the other nitrile-esters of β-methyldicarboxyglutaconic acid will be synthesized by the similar method.

In a previous paper[3] it was shown that the diethyl α-sodio-α, γ-dicyanoglutaconate $C_2H_5OCO(CN)C=CH{-}CNa(CN)COOC_2H_5$ does not yield the corresponding free nitrile-ester on acidifying its aqueous solution, but a semihydrate with the formula $(C_{10}H_{12}O_4N){-}C(=NH){-}NH{-}CO{-}(C_{10}H_{12}O_4N)$ is precipitated as yellow crystals. G. Errera and F. Perciabosco[4] showed that the sodium derivative of triethyl dicyanoaconitate $C_2H_5OCO(CN)C=C(COOC_2H_5){-}$

(1) This journal, **2** (1927), 305.
(2) This journal, **2** (1927), 278.
(3) This journal **2** (1927), 28.
(4) *Ber.*, **34** (1901), 3704.

$CNa(CN)COOC_2H_5$ is transformed into a semihydrate on acidifying its aqueous solution. But the hydration does not take place in the β-methyl compound, i. e. diethyl β-methyl-α, γ-dicyanoglutaconate, as described above.

The compound, represented by the formula $C_2H_5OC(CH_3)=C(CN)-COOC_2H_5$ and designated with the name of ethyl ethoxy-ethylidene-cyanoacetate, is already known as ethyl β-ethoxy-α-cyanocrotonate and synthesized by the action of ethyl iodide on the silver derivative of ethyl α-cyano-acetoacetate.(1) The author has obtained the same substance by the condensation of triethyl orthoacetate with ethyl cyanoacetate by means of acetic anhydride, a reaction analogous to those in which ethoxy-methylene compounds are formed,(2) and has ascertained that the ortho-ester can generally condense with methylene compounds such as ethyl cyanoacetate according to the following equation:

$R'C(OR)_3 + CH_2XY + 2(CH_3CO)_2O = ROCK'=CXY + 2CH_3CO_2R + 2CH_3CO_2H$, where R represents any alkyl group, R′ hydrogen or any alkyl group, and X,Y negative groups such as CN or $COOC_2H_5$.

Condensation of Triethyl Orthoacetate and Ethyl Cyanoacetate by means of Acetic Anhydride. — Preparation of Ethyl Ethoxy-ethylidene-cyanoacetate. The mixture of triethyl orthoacetate, ethyl cyanoacetate, and acetic anhydride in the proportion of 1 mol: 1 mol: 2mols is heated in a flask with a reflux condenser. The cooling water is stopped from running and a tube bent downwards is attached to the top of the condenser, so that the reflux condenser separates acetic anhydride from ethyl acetate formed during the reaction, when the cooling water is sufficiently warm, and the ethyl acetate is cooled to condense in the bent tube and can be collected. When ethyl acetate reaches the required quantity, and distils no more, the content of the flask is distilled at first under the ordinary pressure and then under diminished pressure. The portion distilling at 152.5° under the pressure of 7 mm. is collected. Otherwise the residue in the flask may be recrystallised from alcohol after acetic anhydride and unchanged esters have been driven off by vacuum distillation.

Ethyl ethoxy-ethylidene-cyanoacetate prepared by the above method is colourless crystals, contains 7.66% of nitrogen (the formula requires N= 7.65 %), and, when recrystallised from alcohol a few times, melts at 74–75°. This is the same as ethyl ethoxy-cyanocrotonate synthesized by Haller, and is formed according to the following equation:

$$CH_3C(OC_2H_5)_3 + CH_2(CN)COOC_2H_5 + 2\,(CH_3CO)_2O = CH_3C(OC_2H_5)=C(CN)COOC_2H_5 + 2\,CH_3CO_2C_2H_5 + 2\,CH_3CO_2H.$$

(1) Haller, *Compt. rend.*, **130** (1900), 1223.
(2) *Ann.*, **297** (1897), 1; *Bull. soc. chim.*, [3], **25** (1901), 21.

Condensation of Ethyl Ethoxy-ethylidene-cyanoacetate with Ethyl Sodiocyanoacetate.—Synthesis of Diethyl β-Methyl-α,γ-dicyanoglutaconate. Ethyl ethoxy-ethylidene-cyanoacetate prepared by the above method was added to the equivalent amount of ethyl sodio-cyanoacetate in absolute alcohol. The clear reddish yellow solution was allowed to crystallise at the room temperature. The crystalline substance was collected and recrystallised from absolute alcohol. 0.1875 Gr. of the substance gave 16.85 c. c. of nitrogen at 14°, 758.2 mm. (Found: N=10.50. $C_{12}H_{13}O_4N_2Na$ requires N=10.29%.) This compound is diethyl α-sodio-β-methyl-α, γ-dicyanoglutaconate and the condensation is represented by the equation indicated in page 103. see errata, V.3, P 321

The sodium compound is nearly colourless and very easily soluble in water. The aqueous solution deposited an oily substance on acidifying with dilute hydrochloric acid. This oil was taken with ether, but when the ether was driven away from the solution, it did not remain colourless for a long time and changed into a red crystalline mass. For this reason it was impossible to ascertain the formula of this compound by analysis. (Found: C=56.57,55.91; H=5.68,5.62; N=11.05,11.04. $C_{12}H_{14}O_4N_2$ requires C=57.58; H=5.64; N=11.20%.) That this substance is not a semihydrate is evident from the following facts: (I) It is precipitated immediately when the aqueous solution of the sodium derivative is acidified, and (II) it is soluble in ether.[1] This is diethyl β-methyl-α, γ-dicyanoglutaconate with the formula $C_2H_5OCO(CN)CH\text{–}C(CH_3)=C(CN)COOC_2H_5$.

A silver derivative was obtained in colourless fine crystals when equivalent amounts of the sodium compound and of silver nitrate were mixed in aqueous solutions. It was purified by recrystallisation from alcohol. 0.2953 Gr. of the silver compound gave 0.4319 gr. of CO_2 and 0.0927 gr. of H_2O; 0.2806 gr. of the substance gave 0.4095 gr. of CO_2 and 0.0882 gr. of H_2O; 0.3626 gr. of the substance gave 24.25 c. c. of nitrogen at 15°, 769.3 mm. (Found: C=39.90, 39.81; H=3.51, 3.52; N=7.89. $C_{12}H_{13}O_4N_2Ag$ requires C=40.34; H=3.67; N=7.84%.) These numbers show that the substance could not be perfectly purified by recrystallisation from alcohol.

Another specimen of diethyl sodio-β-methyl-dicyanoglutaconate was prepared by the condensation of ethyl sodiocyanoacetate with ethyl ethoxy-ethylidene-cyanoacetate (ethyl ethoxycyanocrotonate) synthesized from the silver derivative of ethyl cyanoacetoacetate and ethyl iodide, and it was converted into the silver derivative, which was recrystallised from alcohol. 0.2962 Gr. of the substance gave 0.4358 gr. of CO_2 and 0.0948 gr. of H_2O; 0.3449 gr. of the substance gave 23.4 c. c. of nitrogen at 13°, 755.5 mm. (Found: C=40.14; H=3.58; N=7.85. $C_{12}H_{13}O_4N_2Ag$ requires

(1) Cf. this journal, 2 (1927), 29.

C=40.34; H=3.67; N=7.84%.) The latter specimen seems to be purer than the former, and it is probable that the impurity causing the deviation of the analytical result in the former came from the starting substance, i. e. ethyl ethoxyethylidene-cyanoacetate.

The author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART VI.[1]

By **Taku UEMURA and Shozo TABEI.**

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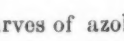
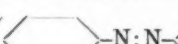
One of the writers[2] has already discussed on the tautomeric transformations of some hydroxyazo-compounds and assigned them different formulas which were derived from the results of alkaline reactions.

We have now to consider the position of the hydroxyl-group with regard to the azo-group, for in a previous report[3] we came to the conclusion that the shape of the absorption bands is probably altered by the insertion of the methyl-group into a benzene nucleus.

But we intend to take another point of view owing to the position of the hydroxyl-group which is included in these compounds. Though our last two papers described this assumption, we shall here again confirm this observation.

Experimental. m-Acetylamino-o-hydroxyazobenzene[4] clearly represents two bands in its absorption curve (Fig. 1). The auxochromic power of the amino-group is nearly lost by acetylation and this is easily understood in comparing the absorption curves of azobenzene (), p-acetylaminoazobenzene[5] () and

(1) Read before the Chemical Society of Japan, February 18, 1928.
(2) Uemura, Yokojima and Tan. this journal, **1** (1926), 260; Uemura, Yokojima and Endo, ibid., **2** (1927), 10 & 48; Uemura and Tabei, ibid., **2** (1927), 229 & 249.
(3) This journal, **2** (1927), 51.
(4) Hewitt and Ratcliffe, *J. Chem. Soc.*, **101** (1912), 1765.
(5) Berju, *Ber.*, **17** (1884), 1400.

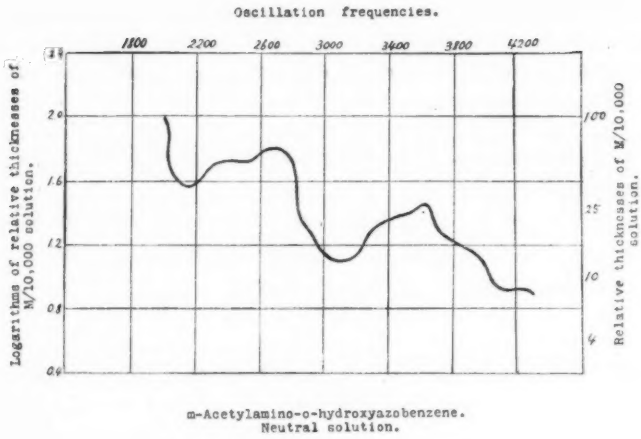
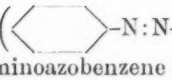


Fig. 1.

p-aminoazobenzene () (Fig. 2). The absorption curve of p-acetylaminoazobenzene approaches to that of azobenzene in the alcoholic solution, while on the contrary p-aminoazobenzene shows the considerable bathochromic influence in its curve. This proves that the auxochromic effect of the amino-group is remarkably weakened when acetylated.

Hence we may conclude that the absorption curve given by the neutral solution of m-acetylamino-o-hydroxyazobenzene is not caused by the acetylamino-group but by the hydroxyl-group. So far as the our studies are concerned, o-hydroxyl with respect to the azo-group has always two absorption bands.

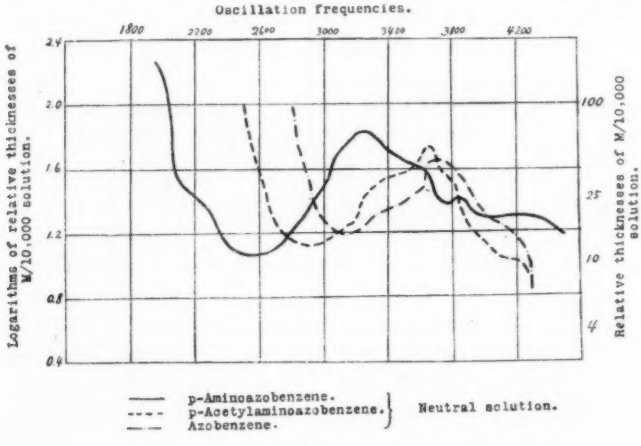


Fig. 2.

The following hydroxyazo-compounds, which appeared in previous papers, have two absorption bands on account of the o-hydroxyl-group with respect to the azo-group.

Benzeneazo-p-cresol.[1]
p-Nitrobenzeneazo-p-cresol.[1]
o-Tolueneazo-p-cresol.[2]
m-Tolueneazo-p-cresol.[2]
p-Tolueneazo-p-cresol.[2]
o-Nitrobenzeneazo-p-cresol.[3]
m-Nitrobenzeneazo-p-cresol.[3]

Summary.

1. The o-hydroxyl-group in hydroxyazo-compounds gives rise to two bands in their absorption curves.

2. The methyl-group shows perhaps no influence upon the shape of the absorption curves of hydroxyazo-compounds.

We wish to express our sincere thanks to Prof. Yuji Shibata of the Tokyo Imperial University for his valuable advice in our researches, and also to the Department of Education and the School for their financial aid throughout our present studies.

Dyeing Department, Tokyo Higher Technical School.

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(1) This journal, **1** (1926), 262 & 265.
(2) Ibid., **2** (1927), 233 & 234.
(3) Ibid., **2** (1927), 256.